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**New Polymers and Processes for Space Applications**

***Final Report***

**15 December 1999 through 30 August 2002**

**Grant No. F49620-00-1-0100**

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## **I. Progress Summary**

The overall objective of this proposal was to conceive and develop new polymeric materials and processes for emerging Air Force applications that are space-based. Specifically, we developed new thermoset materials, including nanostructured and liquid crystalline thermosets, with enhanced use temperature *and* fracture toughness beyond state-of-practice materials. Additionally, we developed new polymer processing methods to achieve concave polymer films with tailored shape. Three distinct thermosetting systems were compared in terms of viability for combined  $T_g$  and fracture toughness enhancement, while maintaining or improving processability over state-of-the-art resin systems. The particular systems studied include: (i) epoxy resins modified by inorganic-organic hybrid POSS compounds, (ii) liquid crystalline thermosets, and (iii) reactive hyperbranched polymeric additives for bismaleimide-polyhedral oligomeric silsesquioxane (BMI-POSS) epoxies. During this program, two graduate assistants were supported, Mr. Haihu Qin (full support) and Mr. Jian Wu (partial support), as well as a postdoctoral researcher, Dr. Gyeong-Man Kim (full support); all through whom significant progress has been made.

## **II. Objectives**

- The overall objective of this proposal was to conceive and develop new polymeric materials and processes for emerging Air Force applications that are space-based.
- We developed new thermoset materials with enhanced use temperature *and* fracture toughness beyond state-of-practice materials.
- We characterized the cure and ultimate properties of the new thermoset materials.

## **III. Accomplishments and New Findings**

(i) **Hybrid Silsesquioxane Thermosets.** During the course of the grant, we successfully set-up a state-of-the-art synthesis laboratory for the preparation and purification of monomers and polymers. Additionally we purchased new characterization equipment (using both AFOSR money and internal funding) that was critical to the program. We investigated the co-curing of purified bismaleimide (BMI) and polyhedral oligosilsesquioxane (POSS)-triorbornene. In the initial stages, we examined the phase behavior of the monomer mixtures and were pleased to find a wide range of miscibility between the monomers. We subsequently examined the cure behavior using DSC, in-situ FTIR, and rheology. We also made significant progress in developing POSS epoxy and BMI thermosets and have studied the cure kinetics thermally and rheologically for both systems. Importantly, we discovered that the thermal properties of POSS-based thermosets are very sensitive to the length of spacer connecting the POSS core to the thermosetting functionality. This work was reported at the Nanostructured Chemicals Workshop and subsequently published in two peer-reviewed journals (see below). Shown below are photographs of POSS-based epoxy samples (left) and POSS-based bismaleimide samples (right) that were prepared for thermal and mechanical analyses. The results were reported in 2 peer-reviewed journal articles and several presentations at national meetings.

G.-M. Kim, H. Qin, X. Fang, F.C. Sun, and PTM, "Hybrid Epoxy-Based Thermosets Based on Polyhedral Oligosilsesquioxane (POSS): Cure Behavior and Toughening Mechanisms," accepted *J. Polym. Sci. B: Polym. Phys. Ed.* (April, 2003).

W. Zhang, B.X.Fu, Y. Seo, E. Schrag, B. Hsiao, PTM, N.-L. Yang, D. Xu, H. Ade, M. Rafailovich, J. Sokolov, "Effect of Methyl Methacrylate/Polyhedral Oligomeric Silsesquioxane Random Copolymers in Compatibilization of Polystyrene and Poly(methyl methacrylate) Blends," *Macromolecules* **35**, 8029-8038 (2002).

P.T. Mather, Invited Lecture, 3<sup>rd</sup> Annual Nanostructured Chemicals Workshop, September 2002, Huntington Beach, CA, POSS-Based Telechelics."

B.S. Kim and P.T. Mather, "Association behavior of nonionic polyhedral oligosilsesquioxane (POSS) telechelics," 74th Annual Meeting of The Society of Rheology, Minneapolis, October, 2002.

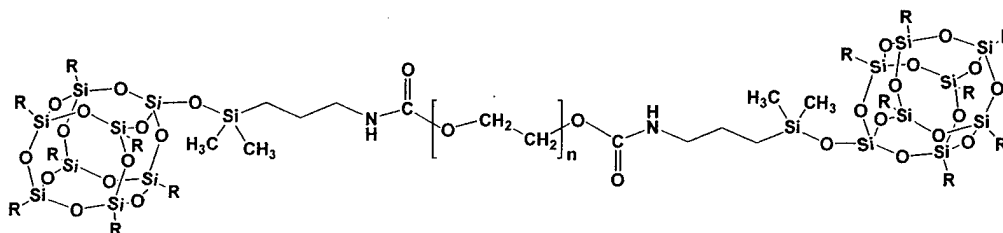


**POSS-Based Epoxy Samples**



**POSS-Based Bismaleimide Samples**

We also developed telechelic POSS materials as toughening additives for epoxies, and this work was reported in *Macromolecules* and was disclosed as an invention. More specifically, polyethylene glycols of varying molecular weight were endcapped with POSS (via urethane linkage) to make difunctionalized telechelics that were found to be compatible with DGEBA/DDS epoxy. An example structure is shown below. Apparent toughening was observed when inspecting the fracture surfaces which became substantially rougher when POSS telechelics were added.



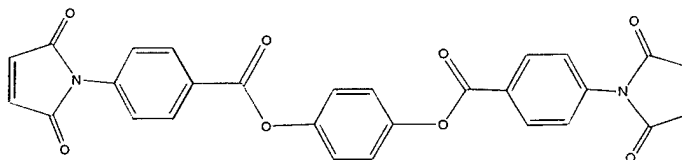
B.-S. Kim and PTM, "Amphiphilic Telechelics Incorporating Polyhedral Oligosilsesquioxane (POSS): 1. Synthesis and Characterization," *Macromolecules*, **35**, 8378-8384, (2002).

P.T. Mather and Byoung-Suhk Kim, "Nonionic telechelic polymers incorporating polyhedral oligosilsesquioxane (POSS) and uses thereof," provisional patent filed (883933.0078) July, 2002. PCT and Conversion, September 2003.

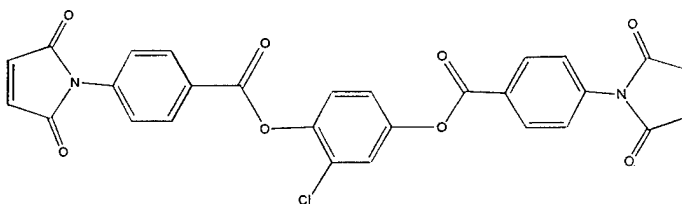
**(ii) Liquid Crystalline Thermosets.**

In the area of liquid crystal thermosets (LCTs), we successfully prepared several new liquid crystalline bismaleimides which were designed to have low melting transition to the nematic phase and cure to nematic solids. The purpose was two-fold: high toughness and excellent barrier properties for chemical propulsion applications. We confirmed, that: (i) we can achieve the structures drawn in the proposal (NMR, FTIR), (ii) nematic phases were formed and preserved in the cured materials, and (iii) the approach using the t-butyl hydroquinone monomer was effective in achieving a low crystal-nematic melting point ( $T_{KN} < 150\text{ }^{\circ}\text{C}$ ). Significantly, chemorheological analysis has revealed that blends containing two or more LCTs differing in their pendant group feature attractive processing windows with melting points in the range of 200-240  $^{\circ}\text{C}$  and cure exotherms in the range 260-290  $^{\circ}\text{C}$ . These findings were reported in 2001 at an MRS meeting on liquid crystals and are part of a manuscript in preparation. The structures that were synthesized and examined in blend form are shown below in Figure 1. The structures with the most promise for future transitions are the MeO-trimer blended with the Cl-trimer – particularly 80:20 Cl/MeO) to give a comparatively low melting point, as shown in a DSC study of Figure 2.

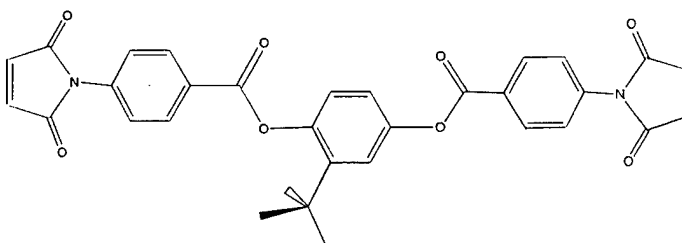
H-trimer



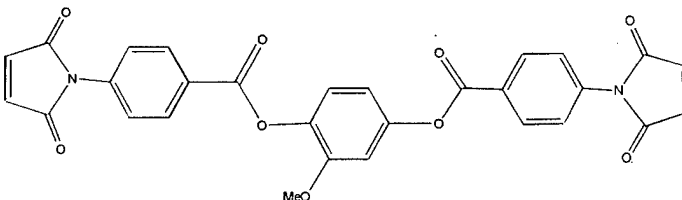
Cl-trimer



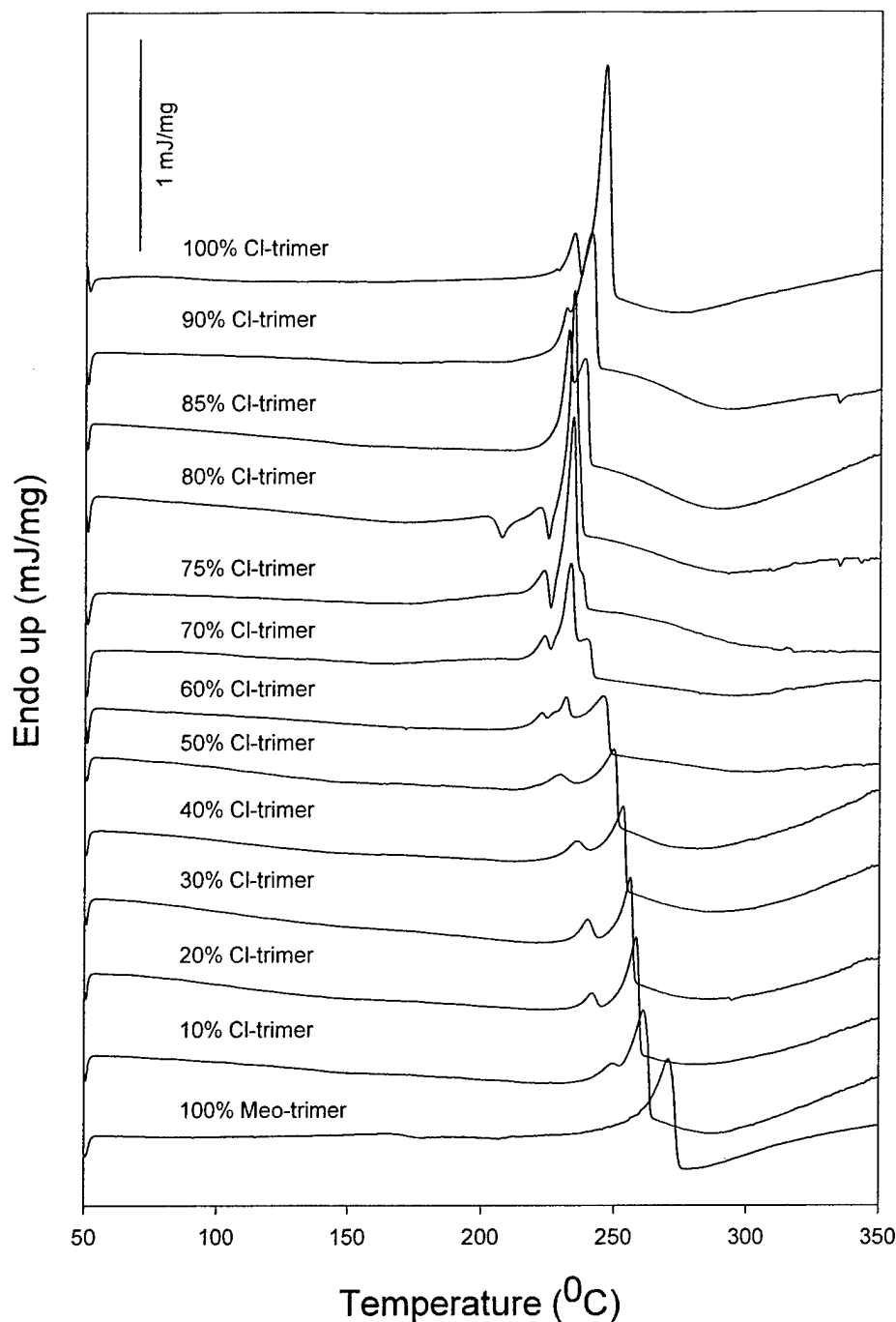
tB-trimer



Meo-trimer



**Figure 1.** LCT "trimers" and their nomenclature.



**Figure 2.** DSC of blends of CI-trimer and MeO-trimer.

H. Qin, PTM, "Optical Rheology of new Liquid Crystalline Thermosets (LCTs): Influence of Shear on Disclination Texture," *Mater. Res. Soc. Proc.* **709** CC8.4.1-7 (2002).

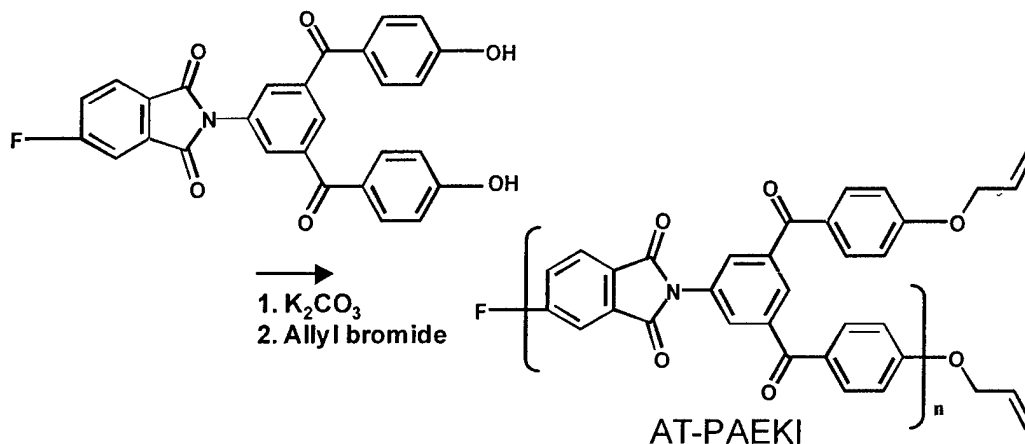
### **(iii) Hyperbranched Thermoset Additives**

Unique hyperbranched polyarylates, poly(aryleneetherketoneimide)s (PAEKI) have been studied in collaboration with Dr. Seng Tan of AFRL/MLBP, their structure being shown in Figure 3 and reported thus far in the following papers:

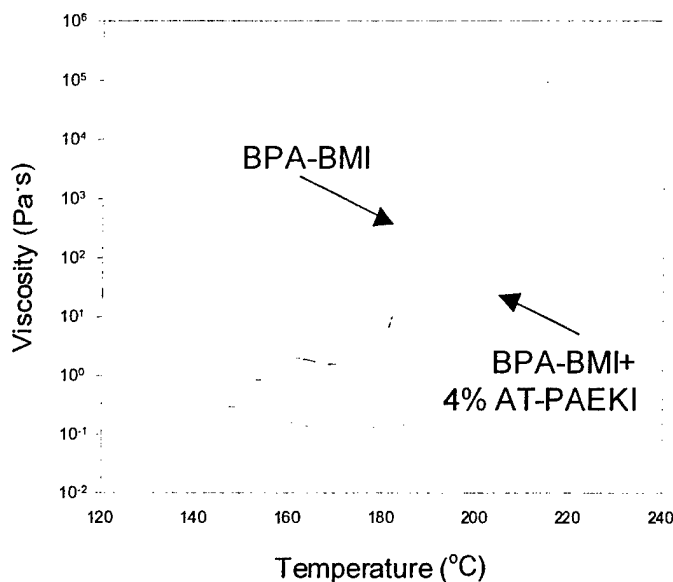
- Jong-Beom Baek, Haihu Qin, Patrick T. Mather and Loon-Seng Tan\*, "A New Hyperbranched Poly(arylene-ether-ketone-imide): Synthesis, Chain-end Functionalization, and Blending with a Bismaleimide," *Macromolecules* **35** 4951-4959 (2002).
- J.-B. Baek, P.T. Mather, and L.-S. Tan, "Synthesis and Chain End Functionalization of a New Hyperbranched Poly(arylene-ether-ketone-imide)," *PMSE Preprints*, **42** (1) (2001).
- J.-B. Baek, J.B. Ferguson, P.T. Mather, and L.-S. Tan, "Hyperbranched Aromatic Polyamides Containing Ether and Quinoxaline Units and Their Blends with BMI," *PMSE Preprints*, **42** (1) (2001).

Unlike other work on hyperbranched polyetherimides these materials incorporate para-carbonyl linkages that facilitate polymerization without additional attachment of silyl leaving groups while adding thermally stable "flexibility". The work of Kwak et al on hyperbranched poly(etherketone)s took similar advantage of this reaction chemistry, but without the incorporation of the thermally stable aromatic imide group. Thus, our system involves the use of only high-temperature linking groups and an all-aromatic structure; this leads to a unique combination of high  $T_g$  and compact hyperfunctional architecture hypothesized to toughen, while maintaining  $T_g$  and decreasing viscosity. While some groups have studied favorable impact of hyperbranched polymers on the toughness of epoxies, while other groups have studied the synthesis and characterization of a similar imide-containing HB-polyarylate. Unique to our approach is two-fold: (i) ketone incorporation that enables avoidance of CsF catalyst, instead polymerizing easily with potassium carbonate, and (ii) tailored functionalization for thermoset curing. Indeed, shown in Figure 3 is the allyl-terminated HBP, AT-PAEKI, with the allyl-ether functionality intended for reactivity in with bismaleimide resins. GPC analysis has allowed estimation of the molecular weight (we discuss below concerns with this analytical method) to be 7000 g/mol, but characterization of the degree of branching was not performed.

We have studied the cure of AT-PAEKI (Allylether Terminated PAEKI) blended with variable loading in the bisphenol-based BMI (BPA-BMI) shown in Figure 4. Importantly, we observed apparent miscibility (clear blends, single  $T_g$ ) over the full composition range for the AT-PAEKI with BPA-BMI, allowing facile characterization of the influence of added hyperbranched polymer on cure behavior and final cured properties. To summarize our initial study of this system, we observe for all blend ratios complete suppression of monomer crystallization (yielding an uncured  $T_g \sim 70^\circ\text{C}$ ), slight increase in cure exotherm, and 65-fold decrease in viscosity minimum for dynamic curing. This latter effect was observed over the full temperature range of the chemorheological experiment, as can be seen in Figure 4, and is attributed to plasticization afforded by the compact HBP additive, as discussed in the introduction section. In addition to this alteration of cure behavior, we observed systematic increase in cured modulus from 2.5 GPa to 4 GPa, as well as indentation hardness, with a maximum at 4 wt-%, as shown in Figure 5. Apparent enhancements of fracture toughness and strength are now being characterized. Thus, we have found a unique combination of attributes of the BPA-BMI/AT-PAEKI (96:4) blend system with simultaneous increase in modulus, decrease in viscosity, increase in toughness, and maintenance of  $T_g$ .



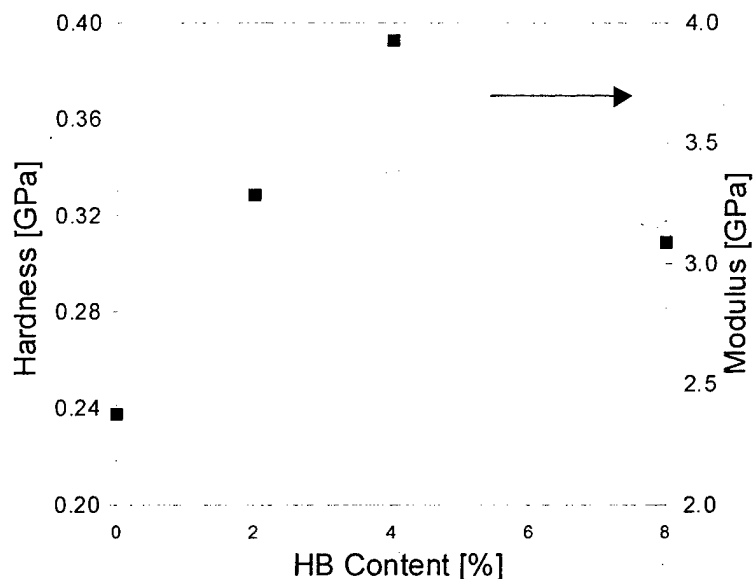
**Figure 3.** Chemical Structure of the imide-ketone  $AB_2$  monomer and functionalized polymer of variable degree of branching (DOB).



**Figure 4.** Viscosity reduction during cure of the BPA-BMI/AT-PAEKI blend system. Dynamic oscillatory shear of 10 rad/sec was used. Two separate runs on neat BPA-BMI are shown for reproducibility.

While we are encouraged by the initial characterization data from this system, much more detailed study is required to understand and optimize the system(s) in order to yield the best balance of viscosity reduction, glass transition temperature, Young's modulus, and fracture toughness. In particular, we have thus far studied AT-PAEKI hyperbranched polymer from single reaction conditions, yielding only one architecture – total molecular weight and degree of branching – despite expectation of a significant impact of HBP architecture on rheological and toughening characteristics.





**Figure 5.** Modulus and hardness increases observed for the BPA-BMI/AT-PAEKI blend system.

#### IV. Summary

Three distinct thermosetting systems were compared in terms of viability for combined  $T_g$  and fracture toughness enhancement, while maintaining or improving processability over state-of-the-art resin systems. The particular systems studied include: (i) epoxy resins modified by inorganic-organic hybrid POSS compounds, (ii) liquid crystalline thermosets, and (iii) reactive hyperbranched polymeric additives for bismaleimide-polyhedral oligomeric silsesquioxane (BMI-POSS) epoxies. The most promising and AF-relevant results were found for approach (iii) and thus this approach is being pursued under a separate AFOSR contract.